METHOD OF PATTERNING A SUBSTRATE

FIELD OF THE INVENTION

[0001] The invention relates to a method of patterning a substrate. In particular, the invention concerns a method of patterning an Indium-Tin Oxide (ITO) film substrate.

BACKGROUND OF THE INVENTION

[0002] Substrates are frequently used in many electronic and telecommunication devices, such as computer chips and mobile phones. Substrates can be made from conductors, semiconductors, superconductors and/or insulators, and the composition of the substrate is usually determined for their suitability for a particular application. For example, ITO has a high electrical conductivity and good optical transparency. These properties make ITO highly suitable for use as transparent conducting electrodes in flat-panel displays, organic light-emitting diodes, and solar cells. ITO may also be used as a sensor for detecting toxic gases. Such applications of substrates usually involve etching into the substrate a desired pattern required for a particular application.

[0003] Several methods have been proposed for etching substrates, including ITO film substrates.

[0004] A method of etching an ITO layer on a substrate is proposed in U.S. Pat. No. 3,979,240. A photoresist corresponding to the desired pattern is laid on the ITO layer to cover or "mask" portions of the ITO layer. The substrate is then immersed in a concentrated solution of hydrobromic acid to etch the unmasked ITO. Another method is proposed in U.S. Pat. No. 5,171,401. A plasma containing methyl radial can effectively etch the ITO film substrate. Selective ion reactive etching is also proposed in U.S. Pat. No. 5,138,664. These methods suffer from the use of certain solutions and/or gases which are harmful to both users and the environment.

[0005] Laser etching of substrates has also been proposed because laser etching does not require photolithography, harmful solutions or gases. One method of laser etching proposed is "dry laser etching" where the surface of the substrate is ablated directly by a laser to pattern the substrate. Dry laser etching is described in several articles, including Yavas O. et al, *High-Speed Maskless Laser Patterning of Indium Tin Oxide Thin Films,* (1998) Appl. Phys. Lett. Vol. 73, No. 18, pp 2558-2560; Yavas, O. et al, *Effect of Substrate Absorption on the Efficiency of Laser Patterning of Indium Tin Oxide Thin Films,* (1999) J. Appl. Phys. Vol. 85, No. 5, pp 4207-4212, and Yavas, O. et al, *Substrate-assisted Laser Patterning of Indium Tin Oxide Thin Films,* (1999) Appl. Phys. A69 (suppl.), s875-s878. As discussed in the first referenced article, dry laser etching has the disadvantage that shoulder-like structures are formed at the rim of the laser irradiated spot. The formation of shoulder-like structures can be attributed to the surface tension gradient in the molten material near the rim.

[0006] Another laser etching method is proposed in U.S. Pat. No. 5,057,184 and Lu, Y. F. et al, *Laser-Induced Etching of Polycrystalline Al_2O_3TiC in KOH Aqueous Solution,* (1996) Appln Phys. A62, pp 43-49. This method is called "wet laser etching" as the substrate is immersed either in an inert liquid or, in an aqueous alkaline or acid solution.

[0007] In the case of wet etching with an inert liquid, laser-induced sonic cavitation of the inert liquid is used to etch the substrate surface. However, wet laser etching using an inert liquid is limited by the need for the substrate to have suitable physical properties for this wet etching method. That is, for the substrate can be effectively etched, the substrate must be able to absorb the laser energy, have a finite melting temperature and must not sublime when being subjected to heat from the laser energy.

[0008] In the case of wet etching with an aqueous alkaline or acid solution, a laser-induced chemical reaction is used to etch the substrate surface. The disadvantage of this wet etching method is that material may be etched at inappropriate locations, even at room temperature.

[0009] In addition, both wet etching methods result in residue or contaminants from the etching process remaining in the solution, and so can be potentially re-deposited on the substrate, causing an undesirable etched pattern.

[0010] Furthermore, a method of laser cleaning an etched substrate has been proposed in Zapka, W. et al, *Efficient Pulsed Laser Removal of 0.2 μm sized particles from a Solid Surface,* (1991) Appl. Phys. Lett. Vol. 58 No. 20, pp 2217-2219; Imen, K. et al, *Laser-Assisted Micron Scale Particle Removal* (1990), Appl. Phys. Lett. Vol. 58 No. 2. pp 203-205, and Tam, A. C. et al, *Laser-Cleaning Techniques for Removal of Surface Particulates,* (1992) J. Appl. Phys. Vol 71 No. 7, pp 3515-3523. These references propose a steam laser cleaning method. A laser is used to irradiate a contaminated substrate with a liquid film deposited on the surface so that the film evaporates to carry away particulate contaminants from the substrate and does not involve ablating or etching the substrate surface. Laser fluence and the number of pulses must be deliberately minimised in the method to prevent any damage to the substrate. In addition, the function of the liquid film is to enhance cleaning efficiency of this method.

SUMMARY OF THE INVENTION

[0011] The present invention provides a method of patterning a substrate according to a predetermined path, said method including forming a liquid film on the substrate surface and directing laser energy from a laser through the film to etch the substrate surface, wherein etched material is carried away from the substrate surface via evaporation of the film during said etching.

[0012] With the present invention, the formation of shoulder-like structures at the rim of the laser-irradiated spot can be effectively avoided, the etching rate is greatly enhanced, and the etched materials can be carried away to prevent possible re-deposition on the substrate. In particular, the laser energy induces sonic cavitation of the liquid film to etch the substrate. Thus, etching and patterning quality can be greatly improved by the method of the invention

[0013] In the context of this specification, the term "liquid film" means a relatively thin layer of liquid with a thickness of micrometer scale.

[0014] After laser patterning, the liquid film is evaporated. A dry substrate with a desired pattern can be observed.

[0015] Preferably, the liquid film is formed on the substrate surface by jetting a liquid vapour onto the substrate surface. The liquid vapour is preferably composed of water, alcohol, inert liquid or non-reactive liquid. In a preferred

DETAILED ACTION

Continued Examination Under 37 CFR 1.114

1. A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114. Applicant's previous and current submission filed on December 16, 2002 and February 14, 2003, respectively, have been entered.

Amendment

2. Amendment filed December 16, 2002 and February 14, 2003 have been entered as Paper No. 28 and 32, respectively. Claims 18 38 and 43 have been amended. Claims 47-52 have been newly added. Claims 1, 4-8, 10, 13-19, 22-28, 36, 38, 39 and 43-52 are pending.

Claim Objections

3. Claims 38, 39, 43 and 44 are objected to because of the following informalities:

Claims 38 and 43 appear to claimed a same matter (500 to 700), and claims 39 and 44 appear to claimed a same matter (600 Torr).

Appropriate correction is required.

Response to Amendment

4. The amendment filed December 16, 2002 is objected to under 35 U.S.C. 132 because it introduces new matter into the disclosure. 35 U.S.C. 132 states that no amendment shall introduce new matter into the disclosure of the invention. The added material which is not

US005643472A

United States Patent [19]

Engelsberg et al.

[11] Patent Number: 5,643,472

[45] Date of Patent: Jul. 1, 1997

[54] **SELECTIVE REMOVAL OF MATERIAL BY IRRADIATION**

[75] Inventors: **Audrey C. Engelsberg**, Milton, Vt.; **Donna R. Fitzpatrick**, Washington, D.C.

[73] Assignee: **Cauldron Limited Partnership**, Bethesda, Md.

[21] Appl. No.: **306,431**

[22] Filed: **Sep. 19, 1994**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 45,165, Apr. 12, 1993, abandoned, which is a continuation-in-part of Ser. No. 865,039, Mar. 31, 1992, abandoned, which is a continuation-in-part of Ser. No. 611,198, Nov. 9, 1990, Pat. No. 5,099,557, which is a division of Ser. No. 216,903, Jul. 8, 1988, Pat. No. 5,024,968.

[51] **Int. Cl.**[6] **B08B 5/00**; B08B 7/00; B23K 26/00

[52] **U.S. Cl.** **216/65**; 216/66; 134/1; 219/121.69; 219/121.84; 204/192.32

[58] **Field of Search** 204/192.1, 192.32; 216/65, 66; 134/1; 219/121.69, 121.84; 156/643.1

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,368,080	1/1983	Langen et al.	134/1
4,393,311	7/1983	Feldman et al.	250/459.1
4,508,749	4/1985	Brannon et al.	216/58 X
4,720,621	1/1988	Langen	219/121.6
4,731,516	3/1988	Noguchi et al.	219/121.66
4,756,765	7/1988	Woodroffe	134/1
4,782,029	11/1988	Takemura et al.	437/11
4,898,650	2/1990	Wu et al.	134/1 X
4,920,994	5/1990	Nachbar	134/1

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

0091646	4/1983	European Pat. Off. .
0497180A2	8/1992	European Pat. Off. .
57-130416	8/1982	Japan .
59-206195	11/1984	Japan .
60-129136	7/1985	Japan .
61-147988	7/1986	Japan .
1018590	1/1989	Japan .
83/01400	4/1983	WIPO .
94/23854	10/1994	WIPO .

OTHER PUBLICATIONS

de Larios J. et al., "Gas–Phase Cleaning of Trace Metal and Organic Contaminants From Wafers: Ultraviolet Irradiated Oxygen–Based and Chlorine–Base Chemistries," *Microcontamination Conference Proceedings*, 1992, pp. 706–717.

Ohmi, T. et al., "Forsightedness in RCA Cleaning Concept and Importance of Surface Microroughness in ULSI Device Performance," *Microcontamination Conference Proceedings*, 1991, pp. 491–510.

Shimono, T. et al., "Device Degradation By Metallic Contamination, and Evaluation and Cleaning of Metallic Contaminants," *Microcontamination Conference Proceedings*, 1991, pp. 544–551.

Van Eck, B. et al., "Vaper Phase Etching and Cleaning of SiO_2," *Microcontamination Conference Proceedings*, 1992, pp. 694–705.

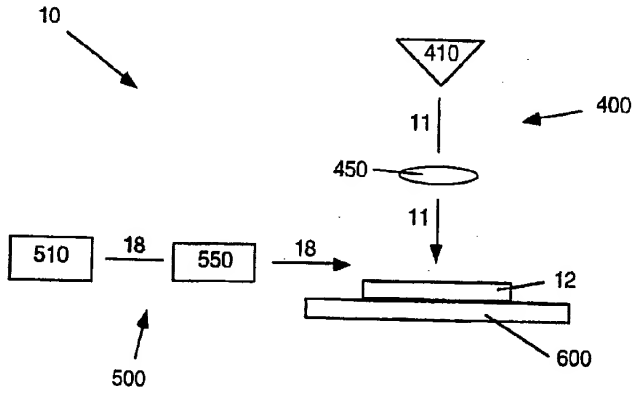
(List continued on next page.)

Primary Examiner—Thi Dang
Attorney, Agent, or Firm—Howrey & Simon

[57] **ABSTRACT**

An apparatus and method for selectively removing undesired material from the surface of a substrate provides a flow of inert gas over the undesired material substrate surface while irradiating the undesired material with energetic photons. The invention enables removal of undesired material without altering the physical properties of the material underlying or adjacent the removed, undesired material. The invention can be applied to produce changes in surface topography (including nano-structuring and surface planarization).

13 Claims, 6 Drawing Sheets



US005958268A

United States Patent [19]

Engelsberg et al.

[11] Patent Number: 5,958,268

[45] Date of Patent: Sep. 28, 1999

[54] **REMOVAL OF MATERIAL BY POLARIZED RADIATION**

[75] Inventors: **Audrey C. Engelsberg**, Milton; **William P. Parker**, Waitsfield, both of Vt.

[73] Assignee: **Cauldron Limited Partnership**, Bethesda, Md.

[21] Appl. No.: **08/609,449**

[22] Filed: **Mar. 1, 1996**

Related U.S. Application Data

[62] Division of application No. 08/472,762, Jun. 7, 1995, abandoned.

[51] **Int. Cl.**[6] **B23K 26/14**

[52] **U.S. Cl.** **219/121.84**; 219/121.85; 134/1

[58] **Field of Search** 219/121.68, 121.69, 219/121.72, 121.84, 121.85; 134/1, 1.3; 216/65, 94; 437/173; 156/643.1; 264/400

[56] **References Cited**

U.S. PATENT DOCUMENTS

Re. 33,777	12/1991	Woodroffe	134/1
4,368,080	1/1983	Langen et al.	134/1
4,752,455	6/1988	Mayer .	
4,784,135	11/1988	Blum et al. .	
4,908,493	3/1990	Susemihl	219/121.72 X
4,980,536	12/1990	Asch et al.	219/121.68
4,987,286	1/1991	Allen .	
5,023,424	6/1991	Vaught	219/121.69 X
5,024,968	6/1991	Engelsberg .	
5,068,750	11/1991	Cook et al.	134/1 X
5,099,557	3/1992	Engelsberg .	
5,114,834	5/1992	Nachshon	216/65 X
5,151,134	9/1992	Boquillon et al. .	
5,151,135	9/1992	Magee et al. .	
5,228,206	7/1993	Grant et al. .	
5,373,140	12/1994	Nagy et al. .	
5,482,561	1/1996	Yeung et al.	134/1
5,499,668	3/1996	Katayama et al.	134/1
5,531,857	7/1996	Engelsberg et al.	134/1 X
5,592,879	1/1997	Waizmann	134/1 X

FOREIGN PATENT DOCUMENTS

0 091 646	10/1983	European Pat. Off. .	
111060	6/1984	European Pat. Off. .	
350021	1/1990	European Pat. Off. .	
2671430	7/1992	France .	
4-288988	10/1992	Japan	219/121.85
51 66784	7/1993	Japan .	
83/01400	4/1983	WIPO .	

OTHER PUBLICATIONS

"Damage-free Laser Ablation Removal of Organic Materials," IBM Technical Disclosure Bulletin, vol. 37, No. 10, p. 453, Oct. 1994.

Tanabe, et al., "Polarization Dependence of Electric Field Intensity Distributions in Photoresist Films," Jpn. J. Appl. Phys. vol. 33, Pt 1, No. 128, 1994.

von Allmen, et al., "Absorption of Laser Light," von Allmen, M., et al., *Laser-Beam Interactions with Materials*, 2nd ed., Springer, 1995, pp. 5–17.

Grill, W., et al, "Excitation of Coherent and Incoherent Terahertz Phonon Pulses in Quartz Using Infrared Laser Radiation," *Physical Review Letters*, vol. 35, No. 9, pp. 588–591, Sep. 1, 1975.

(List continued on next page.)

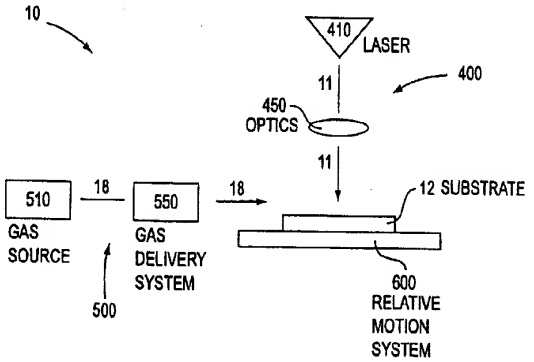
Primary Examiner—Gregory L. Mills

Attorney, Agent, or Firm—Morgan, Lewis & Bockius LLP; C. Scott Talbot; Robert J. Goodell

[57] **ABSTRACT**

An apparatus and method for selectively removing undesired material from the surface of a substrate provides a flow of inert gas over the undesired material substrate surface while irradiating the undesired material with energetic photons. The invention enables removal of undesired material without altering the physical properties of the material underlying or adjacent the removed, undesired material. Removal effectiveness may be enhanced by utilizing polarized energetic photons. Directing a laser beam to the back side of a transparent substrate may enhance the effectiveness of removal.

18 Claims, 6 Drawing Sheets



US006048588A

United States Patent [19]

Engelsberg

[11] Patent Number: 6,048,588

[45] Date of Patent: *Apr. 11, 2000

[54] METHOD FOR ENHANCING CHEMISORPTION OF MATERIAL

[75] Inventor: Audrey C. Engelsberg, Milton, Vt.

[73] Assignee: Cauldron Limited Partnership, Bethesda, Md.

[*] Notice: This patent is subject to a terminal disclaimer.

[21] Appl. No.: 09/039,439

[22] Filed: Mar. 16, 1998

Related U.S. Application Data

[60] Division of application No. 08/472,762, Jun. 7, 1995, abandoned, and a continuation-in-part of application No. 07/611,198, Nov. 9, 1990, Pat. No. 5,099,557, which is a continuation-in-part of application No. 08/306,431, Sep. 19, 1994, Pat. No. 5,643,472, which is a continuation-in-part of application No. 08/045,165, Apr. 12, 1993, abandoned, which is a continuation-in-part of application No. 07/865,039, Mar. 31, 1992, abandoned, which is a continuation-in-part of application No. 07/611,198, which is a division of application No. 07/216,903, Jul. 8, 1988, Pat. No. 5,024,968.

[51] Int. Cl.[7] B05D 3/00

[52] U.S. Cl. 427/554; 134/1; 204/192.32; 216/65; 216/66; 219/121.69; 219/121.84; 427/596

[58] Field of Search 427/595, 596, 427/554; 216/65, 66; 134/1; 219/121.69, 121.84; 204/192.32

[56] References Cited

U.S. PATENT DOCUMENTS

4,172,219	10/1979	Deml et al. .	
4,190,759	2/1980	Hongo et al. .	
4,720,621	1/1988	Langen .	
4,752,455	6/1988	Mayer .	
4,782,029	11/1988	Takemura et al. .	
4,784,135	11/1988	Blum et al. .	
4,843,207	6/1989	Urbanek et al. .	
4,898,650	2/1990	Wu et al. .	
4,987,286	1/1991	Allen .	
5,024,968	6/1991	Engelsberg .	
5,068,750	11/1991	Cook et al. .	
5,099,557	3/1992	Engelsberg .	
5,151,134	9/1992	Boquillon et al. .	
5,151,135	9/1992	Magee et al. .	
5,194,723	3/1993	Cates et al. .	
5,204,517	4/1993	Cates et al. .	
5,228,206	7/1993	Grant et al. .	
5,308,791	5/1994	Horiike et al. .	
5,322,988	6/1994	Russell et al. .	
5,328,517	7/1994	Cates et al. .	
5,373,140	12/1994	Nagy et al. .	
5,376,314	12/1994	Share et al. .	
5,643,472	7/1997	Engelsberg et al.	216/65
5,669,979	9/1997	Elliott et al. .	

FOREIGN PATENT DOCUMENTS

0 091 646	10/1983	European Pat. Off. .
111060	6/1984	European Pat. Off. .
350021	1/1990	European Pat. Off. .
26 71430	7/1992	France .
51-66784	7/1993	Japan .
6-81151	3/1994	Japan .
WO 83/01400	4/1983	WIPO .

OTHER PUBLICATIONS

Dulcey, C., et al., "Deep UV Photochemistry of Chemisorbed Monolayers: Patterned Coplanar Molecular Assemblies," Science, vol. 252, Reports, pp. 551–554, Apr. 26, 1991.

(List continued on next page.)

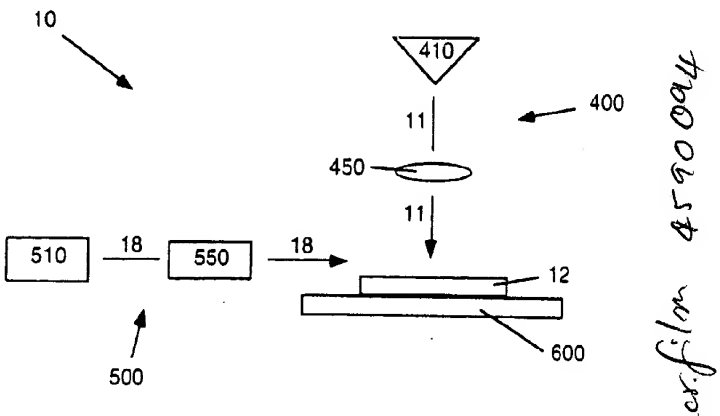
Primary Examiner—Bernard Pianalto

Attorney, Agent, or Firm—Morgan, Lewis & Bockius LLP

[57] ABSTRACT

An apparatus and method for selectively removing undesired material from the surface of a substrate provides a flow of inert gas over the undesired material substrate surface while irradiating the undesired material with energetic photons. The invention enables removal of undesired material without altering the physical properties of the material underlying or adjacent the removed, undesired material. Removal effectiveness may be enhanced by utilizing polarized energetic photons. Directing a laser beam to the back side of a transparent substrate may enhance the effectiveness of removal.

6 Claims, 6 Drawing Sheets



US006038015A

United States Patent [19]

Kawata

[11] Patent Number: 6,038,015

[45] Date of Patent: Mar. 14, 2000

[54] **ELECTRON-BEAM PROJECTION-EXPOSURE APPARATUS WITH INTEGRATED MASK INSPECTION AND CLEANING PORTIONS**

[75] Inventor: **Shintaro Kawata**, Kitasouma-gun, Japan

[73] Assignee: **Nikon Corporation**, Tokyo, Japan

[21] Appl. No.: **09/021,598**

[22] Filed: **Feb. 10, 1998**

[30] **Foreign Application Priority Data**

Feb. 10, 1997 [JP] Japan 9-026739

[51] **Int. Cl.**[7] **G03B 27/54**; A61N 5/00

[52] **U.S. Cl.** **355/67**; 250/492.2

[58] **Field of Search** 355/53, 67; 356/399, 356/400, 401; 250/548, 491.1, 492.2, 492.23, 559.3; 382/144, 149; 430/296; 438/674; 219/121.82

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,980,536	12/1990	Asch et al.	219/121.82
5,043,299	8/1991	Chang et al.	438/674
5,798,196	8/1998	Okino	430/296
5,799,104	8/1998	Nakamura et al.	382/144
5,892,237	4/1999	Kawakami et al.	250/491.1

Primary Examiner—David M. Gray
Assistant Examiner—Peter B. Kim
Attorney, Agent, or Firm—Klarquist Sparkman Campbell Leigh & Whinston, LLP

[57] **ABSTRACT**

Electron-beam projection-exposure apparatus are disclosed that allow a mask pattern to be transferred to a sensitized substrate without defects. An apparatus includes an electron-beam scanner, housed in a vacuum chamber, that scans an electron beam over the mask. As the mask is scanned, an emitted-electron detector senses electrons emitted from the mask at a point of contamination. The contamination is then removed from the mask by a mask-cleaning system, after which the mask is used for exposing a sensitized substrate. The scanner as well as the mask-cleaning system are housed in the same vacuum chamber where projection-exposure of the substrate are performed. Thus, the mask is not exposed to the external environment during inspection, cleaning, and projection-exposure, and inspection, cleaning and projection-exposure of the mask are performed more rapidly than conventionally. The mask-cleaning system, which can utilize a laser beam or a locally delivered reactive gas, cleans the mask at only the points of contamination, rather than the entire mask. Thus, cleaning time is shortened.

38 Claims, 3 Drawing Sheets